Adsorption Capacity of Cu (II) and Pb (II) onto Carbon Fiber Produced from Wool

Fumihiko Ogata, Hisato Tominaga, Moe Kangawa, Kenji Inoue and Naohito Kawasaki

Faculty of Pharmacy, Kinki University, 3-4-1 Kowakae, Higashi-Osaka, Osaka 577-8502, JAPAN

Abstract: The potential utility of the widely available waste product, wool textiles, in the adsorption of heavy metals from industrial and other wastewater systems was investigated by proxy experimentation. Carbon fiber was prepared from dyed wool (DW) by calcination at different temperatures (400, 600, 800, and 1000 °C, referred to as DW400, DW600, DW800, and DW1000, respectively). The samples were analyzed in terms of scanning electron microscope images, percentage yield, specific surface area, pore volume, and the pH of an aqueous suspension of virgin dyed wool (V-DW) or the calcined DW. The adsorption of Cu (II) and Pb (II) from aqueous solutions was studied using the batch method, and the effect of contact time and co-existence of metal ions was investigated. Cu (II) and Pb (II) adsorption increased with increasing DW calcination temperature in the order V-DW < DW400 < DW600 < DW800 < DW1000. The maximum equilibrium adsorption of Cu (II) and Pb (II) achieved with DW1000 (79% and 57%, respectively) was reached within 6 h. Fitting of the adsorption isotherm data for Cu (II) and Pb (II) adsorption onto DW1000 to the Freundlich equation was consistent with monomolecular adsorption onto a heterogeneous surface. The rate-limiting step was determined to be chemical sorption by fitting the adsorption kinetics data to pseudo first-order and pseudo second-order models, given that the pseudo second-order model best fit our data. The study demonstrated that DW1000 was useful for purification of wastewater containing Cu (II) and Pb (II).

Key words: carbon fiber, wool, carbonization, copper ion, lead ion

1 INTRODUCTION

The emergent global concerns of environmental and energy conservation converge on the issue of waste disposal. In Japan, 4.7 million tons of solid waste is generated every year, including 200 thousand tons of textile waste. Approximately 10% of this textile waste is recycled, whereas the remainder is either sent to a landfill or incinerated. Sustainable development requires reduction in the use of landfills and incinerators, and a concomitant increase in the reuse of textile and other wastes.

In addition to solid waste disposal, the removal of heavy metals from groundwater and industrial wastewater is an important environmental concern, with Cu (II) and Pb (II) representing two such heavy metal cation pollutants. Cu (II) is an essential element of the human body; nevertheless, excess Cu (II) can accumulate in brain, skin, liver, pancreas, and myocardium tissues, leading to serious toxicological effects in humans and animals. The standard regulated level of Cu (II) in tap water is less than 1.0 mg/L. Pb (II) is also present as a trace element in the human body; however, excessive intake of Pb (II) causes liver and kidney damage, anemia, headache, encephalopathy, and systemic lead poisoning.

Removal of heavy metals such as Cu (II) and Pb (II) from water systems can be achieved using chemical precipitation, ion exchange, electrolysion, chemical coagulation, membrane processes, evaporation, reverse osmosis, and adsorption. Adsorption represents one of the simplest, most economical, and effective techniques of those generally employed. Recently investigated adsorbents include activated carbon developed from apricot stone, natural zeolite tuff, precursor hazelnut husks, crosslinked chitosan with epichlorohydrin, chitosan-coated sand, Mansonia wood sawdust, and palm shell activated carbon.

The primary motivation of current research is to develop low-cost adsorbents that can be produced from cheap materials such as agricultural and textile wastes; only a few reports have been published on the removal of heavy metals using textile wastes. The production of carbon fiber from textile waste offers two advantages. First, textile
waste is converted to a useful material, i.e., value-added carbon fiber adsorbents, and secondly, the produced carbon fibers may be used for removing heavy metals from aqueous media, such as industrial wastewater.

In this study, carbon fiber was prepared from calcined dyed wool, used as a proxy for textile waste. The prepared carbon fiber was used for adsorption of Cu(II) and Pb(II) from aqueous solution by the batch method. The effect of contact time and co-existence of metal ions on the adsorption process was investigated, and the experimental data obtained were evaluated using equilibrium adsorption isotherms and kinetic models.

2 EXPERIMENTAL PROCEDURES

2.1 Materials
Cu(NO₃)₂, Pb(NO₃)₂, and special-grade NaOH were purchased from Wako Pure Chemical Industries Co., Ltd. Dyed wool was purchased from The Japan Wool Textile Co., Ltd.

2.2 Characteristics of dyed wools (DWs)
Virgin dyed wool (V-DW) was calcined at 400, 600, 800, and 1000°C for 2 h in a muffle furnace. After calcination, scanning electron microscope (SEM) images, percentage yield, specific surface area, base consumption as an index of acidic functional groups, the pH of an aqueous suspension of DW, and pore volume were determined for wool calcined at each temperature (DW400, DW600, DW800, and DW1000).

SEM images were acquired under vacuum using a JSM-5200 (JEOL Ltd.) instrument, after treating the sample surface with osmium tetroxide (OsO₄).

The percentage yield of DW was calculated based on the weight of DW before and after calcination. The specific surface area and pore volume of DW were measured using a NOVA4200e specific surface analyzer (Yuasa Ionics, Japan) based on nitrogen adsorption-desorption isotherms.

The pH of an aqueous suspension of DW was measured by the activated carbon testing method (JIS, K1417).

2.3 Adsorption isotherm
DW (0.05 g, calcined at the various temperatures) was added to 50 mL of Cu(II) or Pb(II) solution at an initial concentration of 500-2000 µg/L. The mixtures were then shaken at 100 rpm for 24 h at 5, 25, and 45°C, and each mixture was filtered using a 0.45-µm membrane filter. The concentration of Cu(II) and Pb(II) in the filtrate was measured using an inductively coupled plasma atomic emission spectrometer (ICP-AES, Shimadzu). The amount of each ion adsorbed was calculated using Eq. (1):

\[ X = \frac{(C_o - C_f) \times (50/1000)}{W} \]

where \( X \) is the amount adsorbed (µg/g), \( C_o \) is the initial concentration (µg/L), \( C_f \) is the equilibrium concentration (µg/L), and \( W \) is the weight of the adsorbent (g).

The pH of each solution was measured using a digital pH meter (Mettler Toledo International Inc.).

2.4 Effect of contact time on the adsorption of Cu(II) and Pb(II)
The effect of contact time on the adsorption of Cu(II) and Pb(II) onto DW was measured in the case of calcination at 1000°C (DW1000) as follows: DW1000 (0.05 g) was added to 50 mL of Cu(II) or Pb(II) solution at an initial concentration of 2000 µg/L. The solution was then shaken at 25°C for 1, 2, 3, 4, 5, 6, 9, 12, 20, and 24 h. The metal ion content of the filtered solutions was measured using ICP-AES. The amount of metal ion adsorbed with time was calculated as above, using Eq. (1).

2.5 Adsorption capacity of Cu(II) and Pb(II) onto DW1000 in binary solution
DW (0.05 g) was added to 50 mL of a binary solution (containing both Cu(II) and Pb(II)) with initial Cu(II) and Pb(II) concentrations of 10 µmol/L. The mixtures were shaken at 100 rpm at 25°C for 24 h. After filtration, metal ions were assayed using ICP-AES. The amount of metal ion adsorbed was calculated as above, using Eq. (1).

3 RESULTS AND DISCUSSION

3.1 Characteristics of dyed wools (DWs)
SEM images of the DWs (Fig. 1) show the morphology of the pores generated on the various calcined dyed-wool (DW400-DW1000) surfaces. The surface pores of DW collapsed with calcination at 1000°C, indicating successful carbonization.

The chemical and physical properties of the DW samples

Fig. 1 SEM images of DWs.
Scale bar is 500 µm.
Adsorption of Cu(II) and Pb(II) onto Carbon Fiber

are shown in Table 1. The percentage yield of DW decreased with increasing calcination temperatures. The highest specific surface area was obtained at calcination temperature of 800°C (DW800 = 226.4 m²/g). However, the largest pore volume was obtained at 1000°C (DW1000 = 0.058 mL/g). Calcination induced a shift in the pH of the supernatant of an aqueous suspension of DW toward basicity (pH = 5.6-6.1), except in the case of DW1000 (pH = 4.0).

3.2 Adsorption isotherm

Equilibrium isotherms for the adsorption of Cu(II) and Pb(II) onto DWs in a single solution system are shown in Fig. 2. The data presented in the isotherms indicate that Cu(II) and Pb(II) adsorption increased with increasing calcination temperature in the order V-DW < DW400 < DW600 < DW800 < DW1000. The respective amounts of Cu(II) and Pb(II) adsorbed onto DW1000 were 828.1 μg/g (at an equilibrium concentration of 1171.9 μg/L) and 1131.9 μg/g (at an equilibrium concentration of 872.7 μg/L). The pH of the respective solutions after adsorption of Cu(II) and Pb(II) fell in the range of 3.68-4.27 and 3.76-4.50; the initial pH values of the respective solutions before adsorption of Cu(II) and Pb(II) were 3.70-4.34 and 3.68-4.42. Even though DW800 exhibited the largest surface area (vide supra), the highest adsorption of both ions was obtained with DW1000 which had the largest pore volume, thus it can be concluded that pore volume was the primary factor governing the amount of Cu(II) and Pb(II) adsorbed based on the data presented in Table 1. Pore volume of DW1000 was greater than that of the other DWs.

Adsorption capacities for Cu(II) and Pb(II) are reported to be 2260 μg/g for Cu(II) using bagasse fly ash and 3190 μg/g for Pb(II) using sawdust\(^\text{10}\). It is anticipated that optimization of the experimental conditions used herein and modification of the adsorbent material should result in a substantial improvement of the adsorption process efficiency.

The amount of Cu(II) and Pb(II) adsorbed onto DW1000 at different temperatures is shown in Fig. 3. The amount of ions adsorbed increased with increasing experimental temperatures, indicating that chemical adsorption may be the governing mechanism for adsorption of Cu(II) and Pb(II) onto DW1000.

The Freundlich equation can be described by assuming a heterogeneous surface with adsorption on each class of sites. The Freundlich equation is described by Eq. (2):

$$\log q_e = \log K + \frac{1}{n} \log C_e$$  \hspace{1cm} (2)

where \(C_e\) is the equilibrium concentration (μg/L), \(q_e\) is the amount adsorbed (μg/g) at equilibrium concentration, and \(K\) and \(1/n\) are the adsorption intensity. The Freundlich constants, \(K\) and \(1/n\), can be determined from a linear plot of \(\log C_e\) versus \(\log q_e\). The constant, \(1/n\), which is the slope of the Freundlich linear equation, numerically represents the affinity of the adsorbent for the adsorbate. The constant, \(K\), which is the intercept of the ordinate, numerically represents the relationship of the adsorbent-adsorbate affinity to which the volume of adsorbate is added\(^\text{11}\). When \(1/n\) falls in the range 0.1-0.5, the adsorbate is considered to be easily adsorbed. On the other hand, if \(1/n > 2\), adsorption is considered to be difficult\(^\text{12}\). The results of the evaluation of the goodness of fit of the experimental data obtained from the adsorption isotherms to the Freundlich

![Fig. 2 Amount of Cu (II) and Pb (II) adsorbed onto DWs at 25°C.](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Percentage yield (%)</th>
<th>Specific surface area (m²/g)</th>
<th>Pore volume (mL/g)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>V-DW</td>
<td>–</td>
<td>0.0</td>
<td>0.001</td>
<td>4.8</td>
</tr>
<tr>
<td>DW400</td>
<td>29.2</td>
<td>0.0</td>
<td>0.000</td>
<td>6.1</td>
</tr>
<tr>
<td>DW600</td>
<td>24.5</td>
<td>68.8</td>
<td>0.000</td>
<td>6.0</td>
</tr>
<tr>
<td>DW800</td>
<td>18.2</td>
<td>226.4</td>
<td>0.007</td>
<td>5.6</td>
</tr>
<tr>
<td>DW1000</td>
<td>11.4</td>
<td>142.3</td>
<td>0.058</td>
<td>4.0</td>
</tr>
</tbody>
</table>

N. D.: Non detected

Table 1 Chemical and physical properties of DWs.
equation model are summarized in Table 2. The values of log \( K \), 1/\( n \), and the correlation coefficient were, respectively, 0.8-2.2, 0.2-0.6, and 0.955-0.974 for Cu(II) and 0.5-2.1, 0.3-0.9, and 0.922-0.964 for Pb(II). The Freundlich plots were linear with correlation coefficients of 0.922-0.974, suggesting agreement with the Freundlich equation. Therefore, it was deduced that Cu(II) and Pb(II) are adsorbed onto DW1000 by a monomolecular adsorption to a heterogeneous surface mechanism.

### Table 2: Freundlich constants and correlation coefficient for adsorption of Cu (II) and Pb (II) by DW1000.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (°C)</th>
<th>Cu (II)</th>
<th>Pb (II)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>l/n</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DW1000</td>
<td>0.6</td>
<td>0.8</td>
<td>0.963</td>
</tr>
<tr>
<td></td>
<td>logK</td>
<td></td>
<td>R</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>2.1</td>
<td>0.939</td>
</tr>
<tr>
<td></td>
<td>R</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.9</td>
<td>0.922</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.9</td>
<td>0.964</td>
<td></td>
</tr>
</tbody>
</table>
3.4 Adsorption capacity of Cu(II) and Pb(II) onto DW1000 in binary solution

The percentage adsorption of Cu(II) and Pb(II) onto DW1000 from a binary solution of the ions is shown in Fig. 5. Herein, the percentage adsorption of either Cu(II) or Pb(II) onto DW1000 in the binary solution system was 45%, whereas in their respective single solution systems, the percentage adsorption was ca. 79% for Cu(II) and 57% for Pb(II) (Fig. 2). The results for adsorption from the binary system show that adsorption of Cu(II) onto DW1000 was comparable with that of Pb(II). DW1000 exhibits a significant adsorption capacity for Cu(II) and Pb(II) even in this binary system, and hence, may be potentially useful for the purification of aqueous solutions containing these heavy metals.

4 CONCLUSION

The results presented herein show that dyed wool (used as a proxy for wool textile waste) calcined at 1000°C (DW1000) can be successfully used to adsorb heavy metal ions from an aqueous solution. Calcination at 1000°C afforded the largest pore volume of the calcined dyed wool samples tested. The adsorption capacity of the samples for both Cu(II) and Pb(II) increased with increasing calcination temperature in the order V-DW < DW400 < DW600 < DW800 < DW1000. Fit of the experimental adsorption data for both ions to the Freundlich isotherm model illustrated that the best description of the metal adsorption mechanism was monomolecular adsorption onto a heterogeneous surface. Moreover, the equilibrium kinetics agreed very well with pseudo-second-order kinetics, which indicated that adsorption occurred by chemisorption. This study shows that the metal ions Cu(II) and Pb(II) are effectively adsorbed from an aqueous system using carbon fiber produced from wool waste. This approach may represent a simple and effective method for re-cycling and adding value to otherwise deleterious textile solid waste in conjunction with cleanup of pollutants from certain kinds of liquid waste such as industrial wastewater.

ACKNOWLEDGEMENT

This work was financially supported by “Antiaging Center Project” for Private Universities from the Ministry of Education, Culture, Sports, Science and Technology, 2008-2012.

References


### Table 3

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Pseudo first-order kinetic model</th>
<th>Pseudo second-order kinetic model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_e$ (μg/g)</td>
<td>$K_1$ (1/h)</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>711.0</td>
<td>0.590</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>1156.6</td>
<td>0.851</td>
</tr>
</tbody>
</table>

Fig. 5 Percentage adsorption of Cu(II) and Pb(II) onto DW1000.

Removal percentage (%)=(Initial concentration–equilibrium concentration)/Initial concentration ×100, Initial concentration of 10 μmol/L.

---

*J. Oleo Sci.* 61, (3) 149-154 (2012)


